Supporting Information
for

A self-template synthesis of defect-rich WS_2 as highly efficient electrocatalyst for hydrogen evolution reaction

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Experimental Section

Preparation of WS_2: Firstly, AMT (0.97 g) was dissolved to deionized water (15 mL). The compound was stirred for 10 min to form a transparent, homogeneous solution at room temperature. According to the ratio of W:S=1:10, 17 mL of ammonium thiosulphate solution (8 wt%) was added. The resultant solution was heated to 70 ^{o}C for 1 h. After cooling to the room temperature, 270 mL of hydrochloric acid is slowly added to generate H_2S gas. The reaction was terminated until the solution turned to reddish brown. The resultant solution was centrifuged three times and the precipitation was placed in a blower dryer at 50 ^{o}C for 5 h. The precursor was ground into a uniform grain size of powder and placed in the tube furnace with Ar/H_2 flow for 30 min. After changing to air flow (60 mL min^{-1}), the precursor was heated to 450 ^{o}C (600 ^{o}C or 750 ^{o}C) for 4 h (5 ^{o}C min^{-1}). The WS_2 template was obtained. Finally, the pure WS_2 nanosheets can be obtained by removing the WO_3 template with 0.1 M NaOH solution.

Electrochemical measurements: The HER performance was measured in 0.5 M H_2SO_4 electrolyte based on a three-electrode cell, in which glass carbon electrode, carbon rod and saturated calomel electrode were used as working, counter and reference electrodes, respectively. 5 μL of catalyst ink were casted onto a glassy carbon electrode with a diameter of 3 mm, and the catalyst loading was 0.283 mg cm^{-2}. LSV curve was recorded with a scan rate of 5 mV s^{-1} and CV was carried out with 50 mV s^{-1} ranging from -0.3 to 0.2 V versus RHE. EIS was measured from 100 kHz to 0.01 Hz by VMP3 potentiostat (Bio-Logic Science Instruments).

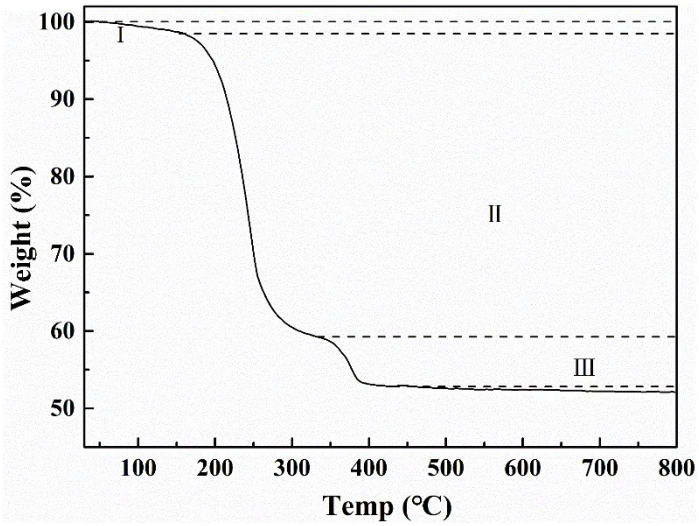

Figure S1 TGA curve of WS_2 precursor.

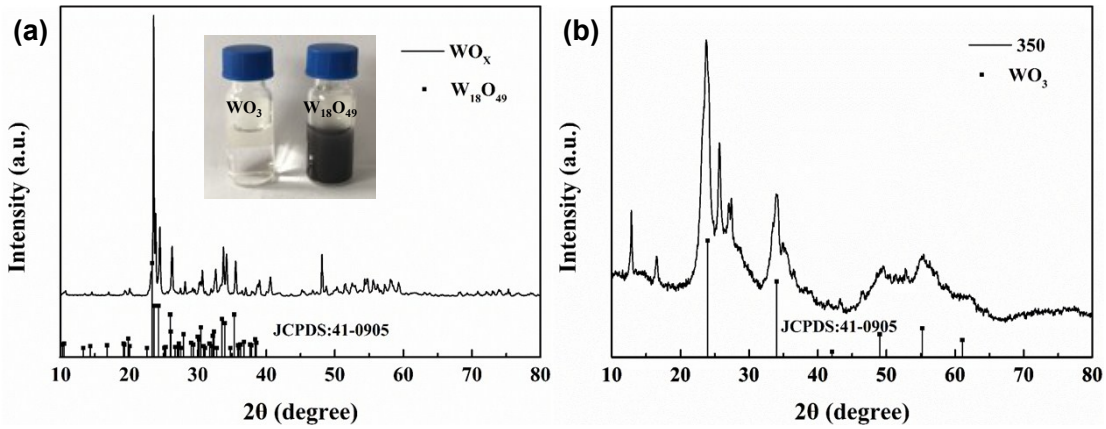

Figure S2 XRD patterns of (a) WS_2 precursor at 750 °C and (b) WO_3 at 350 °C. Dissolution test in 0.1 M NaOH of WO_3 and $W_{18}O_{49}$ was inserted.

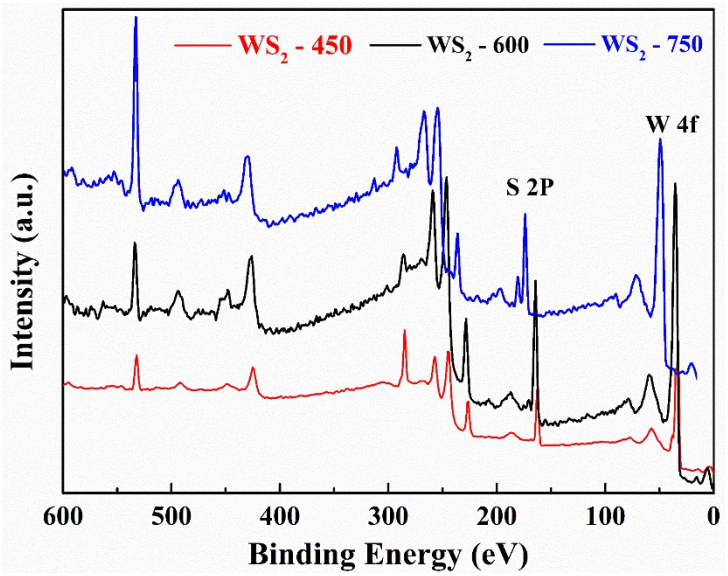

Figure S3 XPS survey scan of WS_2-450, WS_2-600 and WS_2-750 electrocatalysts.

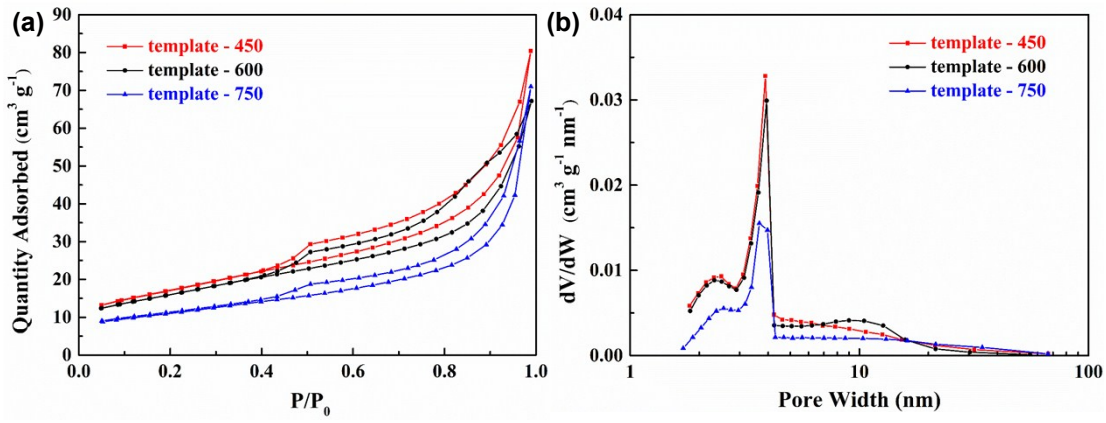

Figure S4 (a) N_2 adsorption-desorption isotherms of WS_2 templates and (b) pore size distributions of WS_2 templates (b) prepared at 450 °C, 600 °C and 750 °C.

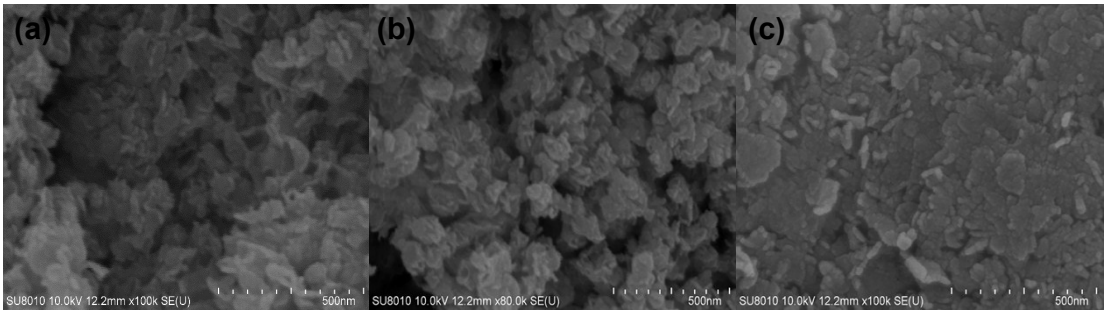

Figure S5 SEM images of (a) WS_2-450, (b) WS_2-600 and (c) WS_2-750 with low magnification.

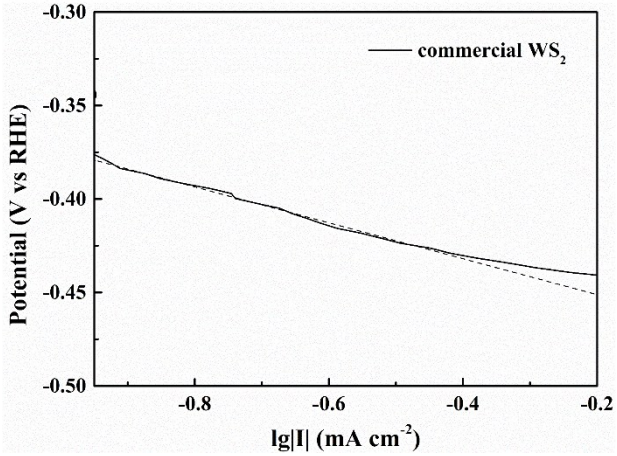

Figure S6 Tafel slopes of commercial WS_2.

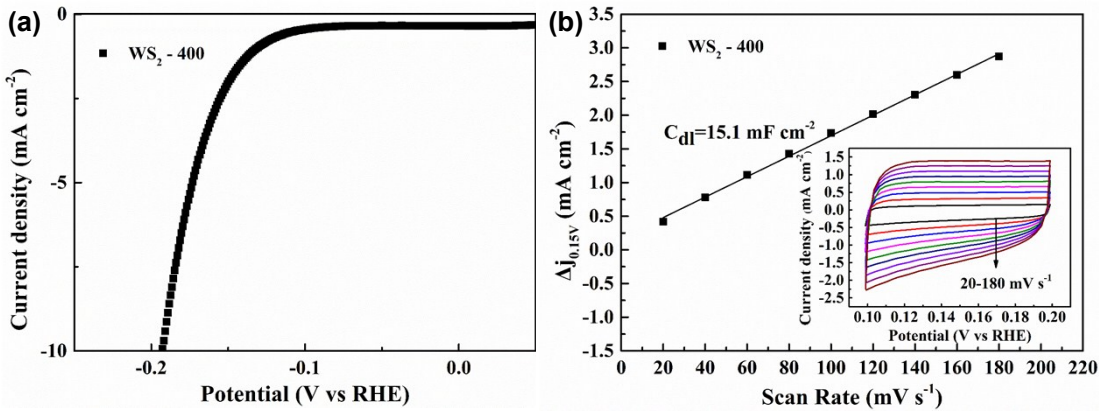

Figure S7 (a) LSV and (b) capacitive current@0.16 V versus RHE as a function of scan rate for of WS_2-400 (CV curves recorded in N_2-saturated 0.5 M H_2SO_4 electrolyte with different scan rates from 20 mV s^{-1} to 180 mV s^{-1} were inserted).

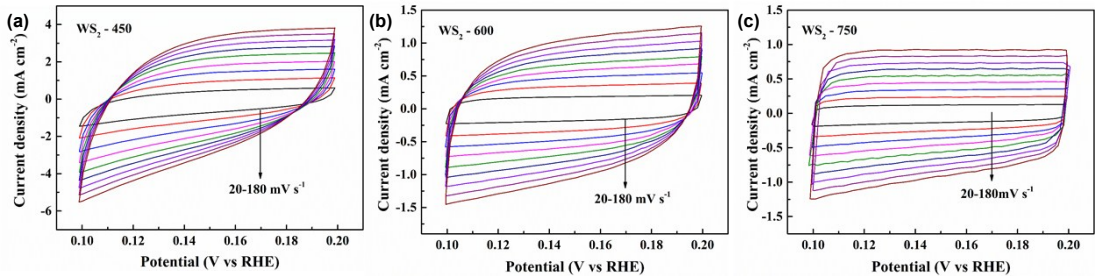

Figure S8 Cyclic voltammetry curves of (a) WS_2-450, (b) WS_2-600 and (c) WS_2-750 recorded in N_2-saturated 0.5M H_2SO_4 electrolyte before durability test with different scan rates from 20 mV s^{-1} to 180 mV s^{-1}.

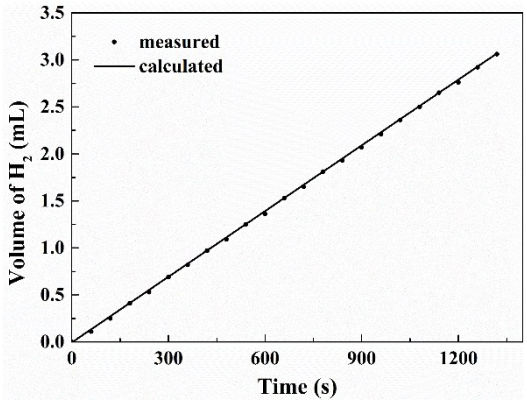

Figure S9 Amount of hydrogen theoretically calculated and experimentally measured versus time for WS_2-450 in 0.5 M H_2SO_4 electrolyte.

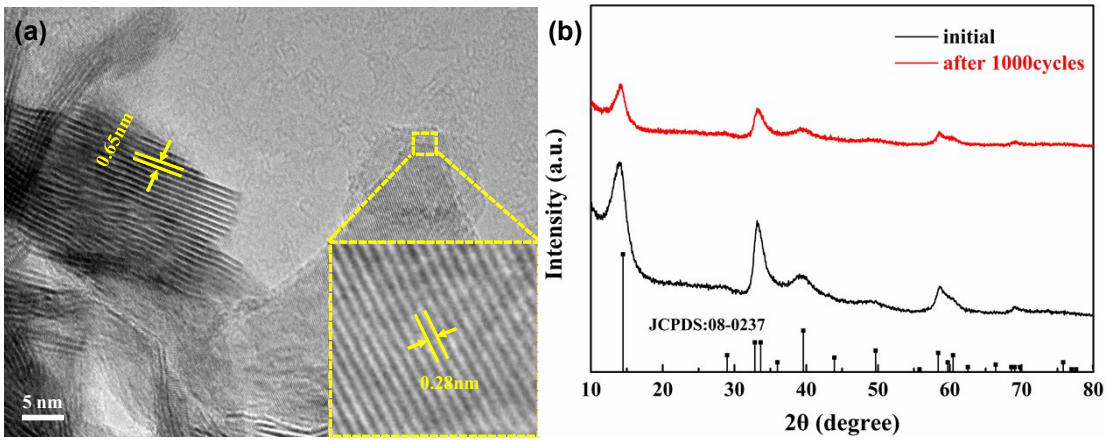

Figure S10 (a) TEM image and (b) XRD patterns of WS_2-450 after durability test.